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CONTENTS:

SOME MOLECULAR WEIGHT DETERMINATIONS, ... *Herbert A. Clark.*

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SOME MOLECULAR WEIGHT DETERMINATIONS,

USING A MODIFIED FORM OF BECKMANN'S BOILING-POINT APPARATUS.

BY HERBERT A. CLARK.

With plate VI.

THE following work was undertaken to test a modified form of Beckmann's boiling-point apparatus, devised and made by Dr. E. C. Franklin.[1] The original intention was to determine the molecular weights of several substances by the boiling-point method, and to compare the results, as well as the accuracy and convenience of manipulation, with corresponding factors for the ordinary Beckmann apparatus, and also to confirm the observations of Franklin and Kraus[2] that the height of the liquid over the bulb of the thermometer has a marked effect on the readings of this instrument.

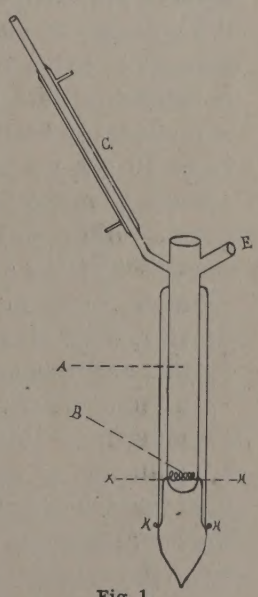


Fig. 1.

The particular piece of apparatus used in this work is represented by figure 1, which is one-sixth natural size. It consists essentially of a Dewar tube, *A*, with a coil of fine platinum wire, *B*, in the bottom, and a water-jacketed condenser, *C*, leading up from the top. The side tube, *E*, allows the insertion of a solute, or of more of the solvent, without disturbing the

1. Franklin and Kraus, Am. Chem. Jour., 20, 836 (1898).
2. Am. Chem. Jour., 20, 839 (1898).

thermometer. Both walls of the vacuum jacket are silvered from the top to the bottom of the inner tube, to prevent radiation, and so the usual platinum cylinder about the thermometer bulb is unnecessary; this avoids differences in concentration in the tube, due to water returned from the condenser. There is a question, however, whether the lack of the platinum cylinder does not cause a slight variable depression of the boiling-point, due to the cooler water from the condenser. Heat is supplied by passing an electric current through coil *B*, which is welded to heavy platinum terminals, *HH*, *KK*, passing through both walls of the Dewar tube. The resistance of the coil at 100° C. is 1.39 ohms.

It is a very simple piece of apparatus to handle, as it is all welded into one piece, with the exception of the outer wall of the condenser; this is removable, as in the ordinary Liebig form. An ordinary Beckmann thermometer, graduated in hundredths, made by F. O. R. Goetze, in Leipzig, was used. When in use, the heating coil was covered to a depth of 2.5 cm. with garnets, and the lower end of the thermometer bulb was put about 1 cm. above the garnets. It was found that a current of 3.8 amperes through the cell would cause 10 c.c. of water, just enough to cover the thermometer bulb, to boil; and that any current from 4.4 to 4.8 amperes (27 to 32 watts) would cause a very steady boiling, with any amount of water in the tube, from 10 c.c. up to 30 c.c. Any greater volume up to 45 c.c., enough to make the water bubble to the top of the Dewar tube, gave a rather variable boiling-point, probably due to the cooling effect of the upper part of the tube which was in contact with the outer air. The current was furnished by a storage battery, was measured with a Weston ammeter reading to tenths, and was controlled by a rheostat.

In the course of a set of readings, the thermometer was read twice with an interval of five minutes, with the same amount of solute and of the solvent; and the average of these two readings was taken as the correct reading for that condition. When the condition was changed by adding more of either the solute or of the solvent, an interval of ten minutes was allowed to let the thermometer become stationary. It was found that the two readings for the same condition rarely differed more than from .001° to .004°, unless there were more than 30 c.c. of liquid in

the tube. The barometer was read between the two readings of the Beckmann thermometer for each condition. The tube was carefully cleaned and dried just before each set of readings. The volume of water was measured with a pipette graduated in tenths. No correction was made for the amount of water clinging to the sides of the tube or of the condenser while the tube was in use. The water used was double distilled from acid and alkaline permanganate solutions, condensed in a block-tin condenser, and kept in a rubber-stoppered Jena flask. No test was made of the purity of the water.

Cane sugar, common salt, and urea are the only solutes investigated so far. The first was a commercial article; the last two were chemically pure, the latter having been made by C. A. F. Kaulbaum. The molecular weight was calculated according to the formula, $M = \frac{Cw}{RW}$; in which w is the weight of the solute in grams; R is the elevation of the boiling-point in degrees; W is the weight of the solvent (assumed to be numerically equal to the volume); and C is the molecular elevation constant for water, obtained from the equation, $C = \frac{2T^2}{L}$, but here assumed to be 520—a value about one per cent. too large at this altitude. The salt and sugar were compressed into pellets to avoid loss in handling, and large crystals of urea were selected for the same reason. As there is about 6.5 volts difference of potential between the ends of the heating coil when the liquid is boiling steadily, the salt was decomposed sufficiently to give a strong odor of chlorine, after the tube and contents were allowed to cool. Thus no dependence is placed on this form of apparatus for work with conducting solutions, and the results obtained with sodium chloride are not here recorded.

As will be seen from table A, the calculated molecular weight of cane sugar varies from 314 to 271 with increasing concentration varying from 17.5 g. of sugar per 100 c.c. of water to 82.6 g. per 100 c.c.; this is much less variation than was obtained by Kahlenberg.[3]

Table B shows the molecular weight of urea, varying from 66.1 with a concentration of 1.51 g. per 100 c.c. of water, to 63.8 with a concentration of 3.03 g., to 64.8 with a concentration of 7.53, and falling to a minimum of 60.4 with a concen-

3. Jour. Phys. Chem., 5, 339 (1901).

TABLE A.—CANE SUGAR.

Barometric variation, 1 mm. Variation of room temperature, 3.6°.

Amount of sugar in 20.27 g. water.	Concentration in grams per 100 c.c.	Boiling-point elevation.	Elevation corrected for barometer and room temp.	Elevation corrected for volume also.	Mol. weight (from column 4).	Mol. weight (from column 5).
1.49 g.	7.35	.119°	.134°	.132°	289	290
3.55	17.5	.286	.298	.290	306	314
5.64	27.9	.459	.475	.465	307	311
7.74	38.1	.653	.669	.657	297	303
10.13	50.1	.868	.884	.869	295	299
12.50	61.8	1.101	1.128	1.108	287	290
14.95	73.8	1.347	1.392	1.368	275	281
16.74	82.6	1.572	1.614	1.586	268	271

TABLE B.—UREA.

Barometric variation, .68 mm. Variation of room temperature, 1.3°.

Amount of urea in 20.12 g. water.	Concentration in grams per 100 c.c.	Boiling-point elevation.	Elevation corrected for barometer and room temp.	Elevation corrected for volume also.	Mol. weight (from column 4).	Mol. weight (from column 5).
.304 g.	1.51	.130°	.119°	.119°	66.1	66.1
.609	3.03	.260	.247	.247	63.8	63.8
.892	4.44	.376	.360	.359	64.1	64.3
1.214	6.04	.510	.490	.488	64.1	64.3
1.513	7.53	.634	.617	.615	64.5	64.8
2.134	10.60	.914	.896	.893	61.5	61.7
2.929	14.55	1.259	1.234	1.230	61.3	61.5
3.771	18.75	1.619	1.606	1.600	60.6	60.8
4.574	22.75	1.977	1.960	1.952	60.4	60.6
5.389	26.80	2.335	2.315	2.305	60.2	60.4

tration of 26.8 g. Dieterici,[4] however, has concluded from his freezing-point determinations that the molecular lowering of the vapor tension of both cane sugar and urea increases with the concentration, between 0.1 and 1.0 normal; while, according to these results, the molecular lowering of the vapor tension in the case of urea *decreases* from a concentration of 3.03 g. per 100 c.c. to 7.53 per 100 c.c. (from .52 to 1.3 normal), and then increases. There is an apparent increase for concentrations less than 3.03 in the case of urea, shown by only two readings; and an apparent *decrease* in the case of cane sugar at a corresponding point. The first reading in each set of readings cannot be depended upon, however, as the probable error is large. The first reading, in most cases, seems to be abnormal when compared with the rest of the readings in the same series.

4. Wied. Ann., 62, 616 (1897).

In both tables, two sets of values for the molecular weight are given: one obtained from data in which the boiling-point elevations are corrected for change of barometer, after the barometer readings have been corrected for change of room temperature; and another in which these two corrections are made, and also another one, depending upon the variation of volume of the liquid, as will be explained farther on. This second set of values is the one referred to in each case in the preceding parts of this paper. None of these corrections are excessive. The first mentioned are so small as to be negligible in the molecular-weight determinations, and the second are not large. According to Landolt and Boernstein, a change of 1 mm. in the height of the barometer causes an appreciable change in the boiling-point of pure water (0.037°), and a change of 1° in the temperature of the barometer produces a change of 0.12 mm. in its readings, between the limits of temperature and pressure observed in this work. The maximum variation of barometer and of room temperature during each set of readings is given at the head of the corresponding table. The molecular-weight determinations were made without using the platinum cylinder.

I have confirmed the observations of Franklin and Kraus, that the boiling-point of the liquid in the tube increased with the amount of liquid present. To ascertain the volume correction, three determinations of the variation of the boiling-point of pure water with the amount of water (see tables C, D, and E) were taken without the platinum cylinder, and two with it (see tables F and G), besides several preliminary determinations. The separate determinations for the same condition are consistent with one another, as will be seen by comparing tables C, D and E with one another, and F with G.

This rise in the boiling-point of a solvent with increasing depth is obviously the effect of the weight of the upper layers of liquid in increasing the temperature of equilibrium between the liquid and vapor phases in the liquid surrounding the thermometer bulb. The rise in pressure due to an increase in the height of water in the tube of one centimeter would raise the boiling-point of the liquid surrounding the thermometer bulb by 0.027°, on the assumption that no mixing of the lower, hotter layers with the upper, cooler ones takes place. In practice, of

course, mixing takes place, with the result that an increase in the height of liquid, while not producing this maximum effect, still brings about a marked rise in the reading of the thermometer.

It was assumed that the volume correction would be the same for a solution as for pure water, which cannot be strictly true if the weight of the supernatant liquid has any influence. It was found that the boiling-point correction due to variable volume is practically negligible in the case of urea, and made a difference of from 1 to 3 per cent. only in the case of sugar. In tables C to E, inclusive, all the corrections mentioned in a preceding paragraph have been applied to the "boiling-point elevations" to give the "corrected elevations." The corrected elevations are the ones used in constructing curves. Tables C and G are taken as typical for the construction of curves (see plate VI).

TABLE C.—WATER.

Barometric variation, .76 mm.
Variation of room temperature, 1.1°.

Amount of water.	Boiling-point elevation.	Corrected elevation.
9.15 c.c.	.000°	.000°
11.25	.000	.004
13.84	.005	.009
16.29	.011	.019
19.53	.004	.015
22.16	.006	.019
25.42	.015	.026
28.58	.024	.038
32.39	.037	.051
35.90	.052	.071
39.33	.062	.080
41.93	.061	.089

TABLE D.—WATER

Barometric variation, .34 mm.
Variation of room temperature, .9°.

Amount of water.	Boiling-point elevation.	Corrected elevation.
9.70 c.c.	.000°	.000°
13.01	.011	.005
16.02	.019	.013
19.40	.024	.016
22.64	.035	.028
25.87	.040	.033
29.11	.051	.040
32.55	.053	.050
36.09	.071	.073

TABLE E.—WATER.

Barometric variation, .72 mm.
Variation of room temperature, 1.5°.

Amount of water.	Boiling-point elevation.	Corrected elevation.
9.86 c.c.	.000°	.000°
13.08	.000	.004
16.13	.001	.012
19.57	.005	.016
22.62	.007	.025
26.10	.013	.034
29.39	.017	.041
32.73	.033	.060
35.89	.041	.067
40.05	.064	.089
43.73	.073	.096

TABLE F.—WATER.

Barometric variation, .44 mm.
Variation of room temperature, 1.7°.

Amount of water.	Boiling-point elevation.	Corrected elevation.
9.63 c.c.	.000°	.000°
12.77	.009	.010
15.52	.019	.028
18.41	.019	.022
21.60	.029	.034
25.03	.044	.054
28.05	.058	.064
31.55	.072	.086
35.09	.088	.102
38.63	.100	.101
42.33	.117	.134

TABLE G.—WATER.

Barometric variation, .50 mm.
Variation of room temperature, 2.1°.

Amount of water.	Boiling point elevation.	Corrected elevation.
9.74 c.c.	.000°	.000°
12.69	.012	.010
15.43	.027	.028
18.86	.023	.031
22.05	.031	.045
25.17	.037	.051
28.27	.051	.065
31.42	.074	.085
34.63	.100	.104
37.69	.121	.120
40.75	.136	.132

TABLE H.—CANE SUGAR.

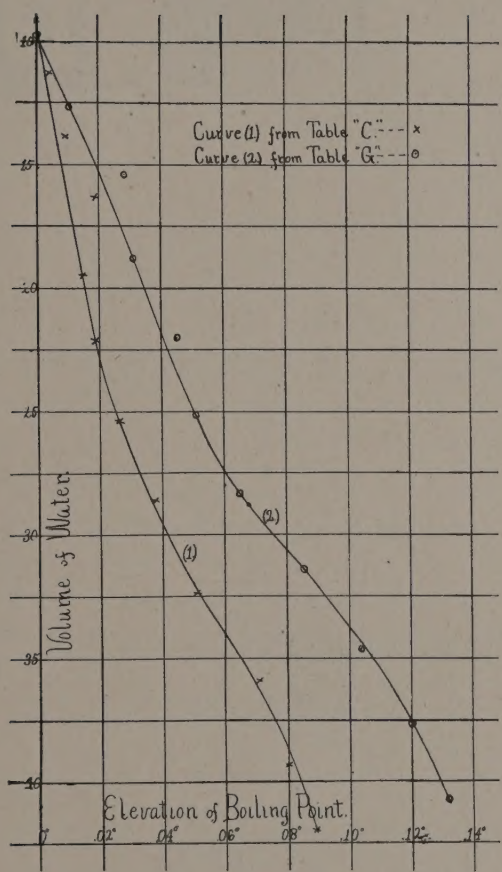
Amount of sugar in one liter of water.	Increase of solution in volume.
75 g.	2.5 %
260	14.8
383	21.8
471	27.4
536	32.0
589	35.1
630	38.0
664	40.0
692	41.8
697	42.3

It was found by trial that the volume of a sugar-water solution varies uniformly with concentration, up to an increase of 42.3 per cent. for a concentration of 14 g. of sugar in 20 c.c. of water (700 g. per liter; see table H). In the case of urea, 5.4 g. in 20 c.c. causes an increase of 19.6 per cent. in the volume.

Column 5, tables A and B, is obtained from column 4 by subtracting from each elevation the elevation due to increase of volume as ascertained from curve 2 and from a straight-line curve showing the increase of volume with concentration, which is obtained from data in the preceding paragraph.

The question of the effect of variation of length, shape and size of the tube, and of the nature of the liquid used, upon the elevation of temperature with increase in amount of liquid, is one that the author expects to take up in the near future. Only one tube has been available as yet, and only one solvent has been used.

PLATE VI.


Curve (1) from Table "C."--- ×
Curve (2) from Table "G"--- ⊙
Volume of Water.
Elevation of Boiling Point.
(1)
(2)
.02°
.04°
.06°
.08°
.10°
.12°
.14°